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Professor Richard Tuckett (University of Birmingham) / July 2011

# The Observation of fluorescence from excited states of $\text{NF}_2$ and $\text{NF}$ following the photodissociation of $\text{NF}_3$ in the 11-30 eV range

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## Abstract

A study of the vacuum-ultraviolet (VUV) fluorescence spectroscopy of  $\text{NF}_3$  in the 11-30 eV range is presented. Synchrotron radiation from BESSY1, Berlin provides the VUV excitation source. Emission due to  $\text{NF } b^1\Sigma^+ - X^3\Sigma^-$  at 528.8 nm is observed between 11.5 and 21.0 eV. Other emissions, which are believed to be due to transitions between highly excited states of  $\text{NF}_2$ , are observed at higher energies, 14.8-24.5 eV. Lifetimes associated with two of these bands at 325 nm and 410 nm are determined to be 12.9 and 13.0 ns, respectively. The similarity of the measured values implies that the two transitions originate from a common upper state.

## 1. Introduction

Due to the use of  $\text{NF}_3$  as a main constituent in some dry etchants, interest has been generated regarding its behaviour when subjected to vacuum-ultraviolet (VUV) excitation. In a series of papers our group has shown that VUV fluorescence spectroscopy can be an extremely useful technique for probing both spectroscopic and dynamic behaviour of the Rydberg states of polyatomic molecules [e.g. 1, 2]. Other groups, using high-energy electrons or radio-frequency (RF) discharges, have sought to diagnose the emissions which are produced following the VUV excitation of  $\text{NF}_3$  [3-5]. The observed emissions were assigned to electronic transitions in  $\text{NF}$ ,  $\text{NF}_2$  and  $\text{F}$ . It should be noted that where  $\text{NF}_2^*$  emission was proposed, the individual states involved were not identified. Fluorescence from either the parent molecule or parent cation was not detected. Although the experiments of these previous workers were largely successful, their progress was hampered by the nature of the excitation sources employed. High-energy electrons and RF discharges are neither well defined nor, in the case of the former, easily tunable. The advantages of synchrotron radiation (SR) are that coverage of the VUV region is complete and tunability, *via* a grating monochromator, is straightforward. By utilising these considerable advantages of SR in the region 10-30 eV, it is the aim of this work to improve the understanding of the processes which occur following the VUV excitation of  $\text{NF}_3$ , and provide useful information for material processing industries.

The  $\text{NF}_3$  molecule belongs to the  $\text{C}_{3v}$  point group and its electronic configuration is  $\dots(3a_1)^2(3e)^2(1a_2)^2(4e)^2(4a_1)^2$ . The numbering scheme does not include the atomic 1s orbitals. The He I photoelectron spectrum has been measured by several groups [6-8], but a photoabsorption spectrum, surprisingly, has not been reported in the literature.

## 2. A review of the electronic spectroscopy of NF<sub>2</sub> and NF

The ground state of the bent (C<sub>2v</sub>) NF<sub>2</sub> molecule has an electronic configuration of ... $(1a_2)^2(4b_2)^2(6a_1)^2(2b_1)^1$ , where the numbering scheme includes all core orbitals. The microwave spectrum of NF<sub>2</sub> was first measured by Brown *et al.* [9], who determined the equilibrium N–F bond length and F–N–F angle of the ground state to be 1.35 Å and 103°20', respectively. The vibrational frequencies have all been measured by infrared (IR) spectroscopy [10]. The excited states of NF<sub>2</sub> are less well characterised. Due to the fact that the closed-shell molecule, N<sub>2</sub>F<sub>4</sub>, exists in equilibrium with NF<sub>2</sub> (N<sub>2</sub>F<sub>4</sub> ↔ 2NF<sub>2</sub>), the measurement of the ultraviolet absorption spectrum of NF<sub>2</sub> is fairly straightforward and Johnson and Colburn [11] have attributed a feature peaking at 260 nm to an electronic transition in NF<sub>2</sub>. Goodfriend and Woods [12] subsequently repeated the experiment and assigned the band to the  $\tilde{A}^2A_1 - \tilde{X}^2B_1$  transition. In addition, vibrational structure was observed corresponding to excitation in the  $\nu_2$  (bend) mode of the excited state with a vibrational frequency of 380 cm<sup>-1</sup>. Several groups have performed *ab initio* calculations on the ground and excited states of NF<sub>2</sub> [13-16]. The most comprehensive study by Cai *et al.* [15] reported equilibrium geometries, excitation energies and vibrational frequencies of the low lying states,  $\tilde{X}^2B_1$ ,  $^2A_1$ ,  $^2B_2$ ,  $2^2A_1$  and  $^2A_2$ , calculated at the HF/6-31 G\* and MP2/6-31 G\* levels. Their results are listed in Table 1. It is worth noting that the  $\tilde{A} - \tilde{X}$  band head is predicted to occur at 277 nm in good agreement with experiment.

An emission spectrum of the NF molecule was first measured by Douglas and Jones [17]. The observed band, with a head at 528.8 nm, was assigned to the  $b^1\Sigma^+ - X^3\Sigma^-$  transition in NF. The radiative lifetime of the  $b^1\Sigma^+$  state was subsequently measured by Tennyson *et al.* [18] to

be  $22.6 \pm 1.7$  ms. More recently Di Stefano *et al.* [19] have recorded a high resolution emission spectrum of the b–X transition and performed a detailed analysis of the line strengths. The  $a^1\Delta - X^3\Sigma^-$  transition was first detected by Jones [20], the band head being located in the near-infrared region at 874.2 nm. Obase *et al.* [21] observed another emission system, in the 440-570 nm region, which they assigned to the NF  $c^1\Pi - b^1\Sigma^+$  transition. With reference to the work of Douglas and Jones [17], the energy of  $c^1\Pi$  relative to the ground state was determined to be  $41698 \pm 3$  cm<sup>-1</sup>. Using this value, Young *et al.* [22] attempted to detect the  $c^1\Pi - a^1\Delta$  transition at 330 nm. Despite the employment of a sensitive laser-induced fluorescence (LIF) technique, they were unsuccessful. The ionisation energy of NF has been determined by Dyke *et al.* [23] to be 12.63 eV.

Many theoretical calculations have been performed to determine the energies of the states of NF [24-28]. The most recent study by Bettendorff and Peyerimhoff [28] yielded potential energy curves for *ca.* twenty states. With the exception of the three lowest states, X, a and b, all of the states were shown to be repulsive and are therefore unlikely to be responsible for the emission of radiation. In addition, some groups have attempted to calculate radiative lifetimes, evaluate line strengths and simulate the form of the various potential energy curves [28-31]. Bettendorff *et al.* [29] have calculated lifetimes of 2.2 s and 18 ms for the  $a^1\Delta$  and  $b^1\Sigma^+$  states, respectively.

### 3. Energetics of the key dissociation channels

The thermochemical dissociation energies ( $\Delta_f H^0$ ) associated with the key fragmentation channels of NF<sub>3</sub> are given in Table 2. Unless otherwise indicated, the species involved are in their ground electronic states. The values were calculated from 0 K heats of formation taken

from the JANAF tables [32]. The energies of the NF b  $^1\Sigma^+$  and F<sub>2</sub> A  $^1\Pi_u$  states are taken from Douglas and Jones [17], and Huber and Herzberg [33], respectively.

#### 4. Experimental

The experiments were performed at the 0.8 GeV synchrotron radiation (SR) source at BESSY, Berlin. The set-up has been described in refs. 1-2. Only brief details are given here. The fluorescence apparatus is attached to the storage ring *via* a 1.5 m normal-incidence monochromator supplying energy-selected photons in the range 11-30 eV. An optical resolution of 0.3 nm is employed. The fluorescence chamber comprises a brass cube (side 5 cm) which is linked to the exit slit of the monochromator *via* two stages of differential pumping. The sample is admitted directly into the fluorescence chamber using a high-precision needle valve. The interaction of the radiation with the gas occurs at the centre of the brass cube. The resulting fluorescence is dispersed by a 20 cm Jobin Yvon H20VIS monochromator (resolution = 8 nm). This ‘secondary’ monochromator operates at atmospheric pressure. Its range of detection is 190-690 nm. The fluorescence is detected by a fast, red sensitive Hamamatsu R6060 photomultiplier tube (PMT). Data acquisition and scanning of the two monochromators are controlled by a dedicated personal computer (PC). The sample was manufactured by Fluorochem. It was supplied in a pressurised lecture bottle and used without further purification.

In the multi-bunch mode of the synchrotron three experiments are performed. First, the energy of the SR ( $E_1$ ) is scanned whilst the secondary monochromator is set to zero order. This mode of operation results in a fluorescence excitation spectrum. Second,  $E_1$  is set to a single value and the wavelength ( $\lambda_2$ ) of the secondary monochromator is scanned. A dispersed fluorescence spectrum is obtained. Third, action spectroscopy is performed by scanning  $E_1$

and setting  $\lambda_2$  to a single value corresponding to the position of an emission band. From such spectra, appearance energies (AEs) associated with a particular excited species, can be obtained. Comparison with thermochemistry may then provide information regarding the nature of the dissociation pathway. In the single-bunch mode of the synchrotron where the molecules are only excited every 208 ns, it is possible to perform time-resolved fluorescence measurements. The measured fluorescence decays are analysed by a non-linear least-squares fitting program. Lifetimes of the various emitting states are obtained. This procedure is described in detail in reference 2. The range of lifetimes that can be measured is limited by the response time of the PMT and the repetition rate of the pulsed excitation source. Accurate values are only obtained in the range 4-80 ns.

## 5. Results

A fluorescence excitation spectrum was measured from 10-30 eV, at a resolution of 0.3 nm. (Fig. 1) All peaks observed, have a shape which is characteristic of a resonant primary photoexcitation process ( $A + h\nu \rightarrow A^*$ ). It is likely, therefore, that the observed emission is caused by electronic transitions in neutral fragment species. The peak positions for bands I-VII in Fig. 1 are 11.4, 13.0, 13.6, 15.2, 17.4, 19.0 and 22.5 eV, respectively. Bassett and Lloyd [7] have reported a He I PES with peaks at 13.73 ( $4a_1$ )<sup>-1</sup>, 16.15 / 16.55 ( $4e$ )<sup>-1</sup>/( $1a_2$ )<sup>-1</sup>, 17.52 ( $3e$ )<sup>-1</sup> and 19.71 eV ( $3a_1$ )<sup>-1</sup>. Calculations using MOLPRO [34] show that the  $4a_1$  HOMO orbital is essentially a nitrogen lone-pair orbital, whilst the  $4e$ ,  $1a_2$  and  $3e$  set have predominantly fluorine lone-pair character. The  $3a_1$  electrons form an N-F  $\sigma$  bond. In principle, then, the features in the fluorescence excitation spectrum may be assigned to transitions to individual Rydberg states using Bassett and Lloyd's ionisation energies, the Rydberg formula, and the accepted quantum defects for the nitrogen and fluorine atoms. In a recent publication [2], however, this procedure was shown to be fraught with difficulties, and



best applied only to absorption spectra. Hence, only semi-quantitative assignments are given here. It is likely that band I arises from excitation to Rydberg states converging on the  $(4a_1)^{-1}$  ionisation energy, whilst bands II/ III, IV and V arise from excitation to states converging on the  $(4e)^{-1}$  /  $(1a_2)^{-1}$ ,  $(3e)^{-1}$  and  $(3a_1)^{-1}$  thresholds, respectively. The transitions at higher energies must represent transitions to Rydberg states converging on higher ionisation energies

Dispersed fluorescence spectra were recorded from 200-550 nm at excitation energies ( $E_1$ ) of 13.6, 18.2 and 22.6 eV (Fig. 2). In all cases, the spectral resolution employed was 8 nm. For  $E_1 = 13.6$  eV, the spectrum consists of one feature at 525 nm. This narrow emission band is assigned to the  $b^1\Sigma^+ - X^3\Sigma^-$  transition in NF (528.8 nm), first detected by Douglas and Jones [17]. At 18.2 eV, the dispersed fluorescence spectrum consists of four broad bands, in addition to the NF  $b^1\Sigma^+ - X^3\Sigma^-$  feature. Peaks are observed at 300, 325, 410 and 450 nm. We believed these are caused by transitions between excited states of  $NF_2$ . The proposed assignments are discussed in Section 6.

Action spectra were recorded from 11-30 eV for emission wavelengths of 292, 325, 410, 448 and 529 nm (Figs. 3 and 4). The appearance energies (AE) are  $15.5 \pm 0.5$ ,  $14.8 \pm 0.4$ ,  $14.8 \pm 0.4$ ,  $16.0 \pm 0.5$  and  $11.5 \pm 1.0$  eV, respectively. The action spectra at 325 and 410 nm are extremely similar. We believe that what appears to be a secondary threshold at *ca.* 22 eV in Figs. 3a, b and 4a merely reflects the change in cross section for the primary excitation process at this energy (see the onset of band VII in Fig. 1), and does not, therefore, represent the onset of a second dissociation channel. A summary of the range of excitation energies,  $E_1$ , and emission wavelengths,  $\lambda_2$ , for each emission band is given in Table 3.

Lifetime measurements were made for three of the emission bands, at 325, 410 and 529 nm (Fig. 5). In general, the excitation energies were chosen on the basis of highest fluorescence count rate. At 325 and 410 nm, a lifetime of *ca.* 13 ns is measured. The fact that identical values are obtained for the two bands strongly suggests that the same upper state is involved in both cases. The lifetime obtained for NF b  $^1\Sigma^+$ ,  $> 100$  ns, is not inconsistent with the pulsed discharge measurement of Tennyson *et al.* [18], 22.6 ms, and the *ab initio* calculation of Bettendorff *et al.* [29], 18 ms. Lifetimes associated with the weaker bands at 292 and 448 nm were not measured because the count rates were too low.

## 6. Discussion

In Section 5, the 528 nm band was assigned to NF b  $^1\Sigma^+ - X^3\Sigma^-$ , whilst the other four broader bands were attributed to transitions between excited states of the NF<sub>2</sub> molecules. The aim of this section is to justify the assignments and attempt to make them more precise. Since the fluorescence excitation spectrum (Fig. 1) contains only resonant features, the fluorescing species must all be neutral fragments formed by the (pre-)dissociation of Rydberg states of NF<sub>3</sub>. The possible candidates are N\*, F\*, F<sub>2</sub>\*, NF\* and NF<sub>2</sub>\*. The atomic species can be eliminated as every feature (Fig. 2), has a full-width at half maximum (FWHM) greater than 16 nm. This leaves F<sub>2</sub>\*, NF\* and NF<sub>2</sub>\*. First, the diatomic fragments will be considered. The spectroscopy of the F<sub>2</sub> molecule is well known up to the K  $^1\Pi_u$  state [33]. The only band in F<sub>2</sub> that fits to one of those observed in the dispersed fluorescence spectra (Fig. 2) is the A  $^1\Pi_u - X^1\Sigma_g^+$  transition (maximum = 285 nm) [33]. The appearance energy (AE) of the 292 nm emission is  $15.5 \pm 0.5$  nm, whilst the  $\Delta H_{rxn}$  associated with the highest energy channel for producing F<sub>2</sub> A  $^1\Pi_u$  is 11.33 eV. This shift does not of course rule out the possibility that F<sub>2</sub> A  $^1\Pi_u$  is emitting. State-specific fragmentation favouring another channel or a high reverse activation barrier along the exit channel of the potential energy surface could prevent the

formation of  $F_2 A^1\Pi_u$  between 11.33 and 15.5 eV. The magnitude of the discrepancy, however, renders these possibilities unlikely for this type of system.

The spectroscopy of NF was reviewed in Section 2. It is extremely likely that the band observed at 525 nm (Fig 2a) is that identified by Douglas and Jones [17], and assigned to NF  $b^1\Sigma^+ - X^3\Sigma^-$ . The AE is  $11.5 \pm 1.0$  eV compared to a maximum  $\Delta_r H^0$  for NF  $b^1\Sigma^+$  state formation of 7.83 eV. In the previous paragraph, a discrepancy of a similar magnitude was used to discount the possibility of  $F_2$  emission for the 290 nm emission band. Here, the situation is different, since an inspection of the fluorescence excitation spectrum (Fig. 1) reveals that there is no signal below 11.5 eV. This indicates that the oscillator strength associated with the primary excitation process below this energy is probably very low. To confirm this theory an absorption spectrum is required. Unfortunately, this measurement has not been made. It is believed, therefore, that the disagreement of the AE and the thermochemical threshold is meaningless, and that in all probability the emission band is NF  $b^1\Sigma^+ - X^3\Sigma^-$ . Indeed, two other observations support this assignment. First, Hargis and Greenberg [5], observed an identical band in a 10 Watt RF discharge of  $NF_3$  which was assigned to NF  $b^1\Sigma^+ - X^3\Sigma^-$ . Second, Tennyson *et al.* [18] measured the lifetime of NF  $b^1\Sigma^+$  to be 22.6 ms, consistent with the flat decay observed in the time resolved fluorescence experiment (Fig. 5c). The  $a^1\Delta - X^3\Sigma^-$  band at 842 nm is outside the region of detection, and Bettendorff and Peyerimoff [28] have predicted that the higher states of NF are all repulsive. Hence, it is unlikely that any of the other emission bands are caused by transitions in NF. Conversely, Obase *et al.* [21] have observed emission at *ca.* 460 nm, and assigned it to the  $c^1\Pi - b^1\Sigma^+$  transition in NF. Their criteria for the assignment, however, is dubious, and the band could just as easily be due to  $NF_2^*$ . Indeed, neither the *ab initio* work of Ellis and Banyard [27] nor Bettendorff and Peyerimoff [28] predict a transition in this region or

identify the c state as possessing a  $^1\Pi$  term symbol. It is our belief, therefore, that the four features below 500 nm are not due to NF.

Since four of the observed emission bands are not caused by transitions in either NF\* or F<sub>2</sub>\*, NF<sub>2</sub>\* must be involved. The spectroscopy of NF<sub>2</sub> has been reviewed in Section 2. The  $\tilde{A}^2A_1 - \tilde{X}^2B_1$  transition, at *ca* 260 nm, could be responsible for the lowest-wavelength emission band at *ca* 290 nm. The thermochemical threshold, however, for producing the  $\tilde{A}^2A_1$  state of NF<sub>2</sub> is 7.34 eV, compared with an AE for the 300 nm emission band of 15.5±0.5 eV. This discrepancy is so large that it is unlikely that NF<sub>2</sub>  $\tilde{A}^2A_1$  is emitting. The AEs for all four emission bands lie in excess of 14.8 eV. Since the thermochemical threshold for producing ground-state NF<sub>2</sub> is 2.57 eV, it is likely that the NF<sub>2</sub>\* emitters lie at least 12.23 eV above the ground state. These highly excited states have never been identified experimentally, and the *ab initio* calculations of Cai *et al.* [15] only extend to the  $\tilde{D}^2A_2$  state, *ca* 7 eV above the ground state. The lack of a suitably comprehensive set of *ab initio* calculations, available for comparison with the fluorescence spectra, is in contrast with our study on PF<sub>3</sub> [1]. Latifzadeh and Balasubramanian have calculated energy levels for PF<sub>2</sub> up to the  $\tilde{G}^2A_2$  state [35]. This made it possible for the  $\tilde{E} - \tilde{A}$ ,  $\tilde{C} - \tilde{X}$ ,  $\tilde{B} - \tilde{X}$  and  $\tilde{A} - \tilde{X}$  transitions in PF<sub>2</sub> to be identified in the dispersed fluorescence spectra of PF<sub>3</sub> [1]. Since these calculations have not been performed for NF<sub>2</sub>, the emission bands cannot be assigned to particular transitions.

The following comments can, however, be made. A combination of the thermochemistry, appearance energies and the calculations of Cai *et al.* [15] indicates that the emitting state involved in each transition lies above the  $\tilde{D}^2A_2$  state. Due to the similarity of the action spectra associated with the 325 nm and 410 nm bands, and the fact that the measured

lifetimes, 13 ns, and AEs,  $14.8 \pm 0.4$  eV, are identical, it seems reasonable to conclude that the upper state involved in both transitions is the same. Furthermore, the magnitude of the lifetime indicates that the transitions are both formally allowed. Since the emission bands at 290 and 450 nm have higher appearance energies,  $15.5 \pm 0.5$  and  $16.0 \pm 0.5$  eV respectively, it is likely that the emitting states lie at higher energy than that of the 325 and 410 nm bands. Unfortunately it was not possible to measure the lifetimes associated with emission at either 325 nm and 410 nm. The action spectra at these two wavelengths are also sufficiently different to discount the involvement of a common state of  $\text{NF}_2$  being responsible for these two emission bands.

## 7. Conclusions

A study of the VUV fluorescence spectroscopy of  $\text{NF}_3$  has been presented. Emissions have been assigned to transitions between excited states of  $\text{NF}$  and  $\text{NF}_2$ , produced by (pre-)dissociation of the Rydberg states of  $\text{NF}_3$ . In contrast with previous work, using high energy electrons (200 eV) [3, 4], there is no evidence of F emission, presumably because the excitation energy ( $E_1 < 30$  eV) is too low. The lack of comprehensive *ab initio* calculations in the literature has prevented the assignment of the  $\text{NF}_2$  emission bands. In turn, due to the lack of assignments, the dynamical information that can be inferred from the AEs is extremely limited. Of greatest interest, perhaps, is the fact that  $\text{NF } b \ ^1\Sigma^+$  emission is observed at lower excitation energies than  $\text{NF}_2^*$  emission. This leads to two possible conclusions. Either, at excitation energies below 14.5 eV state-specific fragmentation favouring the formation of  $\text{NF } b \ ^1\Sigma^+$  occurs, or, in contrast to the  $\text{PF}_2$  radical [1],  $\text{NF}_2$  produced in low excited states, ( $\tilde{\text{A}} - \tilde{\text{D}}$ ), does not fluoresce.

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## ***List of Tables***

**Table 1** The energies and geometries of the ground and first few excited states of  $\text{NF}_2$  determined by *ab initio* calculations. The data is taken from Cai *et al.* [15]

**Table 2** Energetics of the key dissociation channels of  $\text{NF}_3$ .

**Table 3** Summary of the emission bands observed following the photoexcitation of  $\text{NF}_3$ .

**Table 1**

Electronic state	Configuration	R(N–F) Å	F–N–F Angle / deg	Energy / eV
$\tilde{X}^2B_1$	$\dots(1a_2)^2(4b_2)^2(6a_1)^2(2b_1)^1$	1.317	103.3	0
$\tilde{A}^2A_1$	$\dots(1a_2)^2(4b_2)^2(6a_1)^1(2b_1)^2$	1.342	120.1	4.470
$\tilde{B}^2A_1$	$\dots(1a_2)^2(4b_2)^2(6a_1)^2(7a_1)^1$	1.484	145.4	5.284
$\tilde{C}^2B_2$	$\dots(1a_2)^2(6a_1)^2(4b_2)^1(2b_1)^2$	1.539	75.9	5.560
$\tilde{D}^2A_2$	$\dots(1a_2)^1(4b_2)^2(6a_1)^2(2b_1)^2$	1.530	85.8	7.825

**Table 2**

Fragmentation channel	Dissociation energy / eV
$F_2 A \ ^1\Pi_u + N + F$	11.33
$N + 3F$	8.59
$NF b \ ^1\Sigma^+ + 2F$	7.83
$N + F_2 + F$	6.99
$NF b \ ^1\Sigma^+ + F_2$	6.23
$NF + 2F$	5.49
$NF + F_2$	3.89
$NF_2 + F$	2.57

**Table 3**

<b>Emitter</b>	<b>Threshold / eV</b>	<b>E<sub>1</sub> range / eV</b>	<b>λ<sub>2</sub> range: (peak position) / nm</b>	<b>Assignment</b>
NF b $^1\Sigma^+$	11.5±1.0	11.5-21.0	515-540: (529)	b $^1\Sigma^+$ -X $^3\Sigma^-$
NF <sub>2</sub> *	14.8±0.4	14.8-23.5	280-360: (325)	-
NF <sub>2</sub> *	14.8±0.4	14.8-23.5	360-440: (410)	-
NF <sub>2</sub> *	15.5±0.5	15.5-24.5	260-340: (292)	-
NF <sub>2</sub> *	16.0±0.5	16.0-23.5	420-480: (448)	-

## ***Figure Captions***

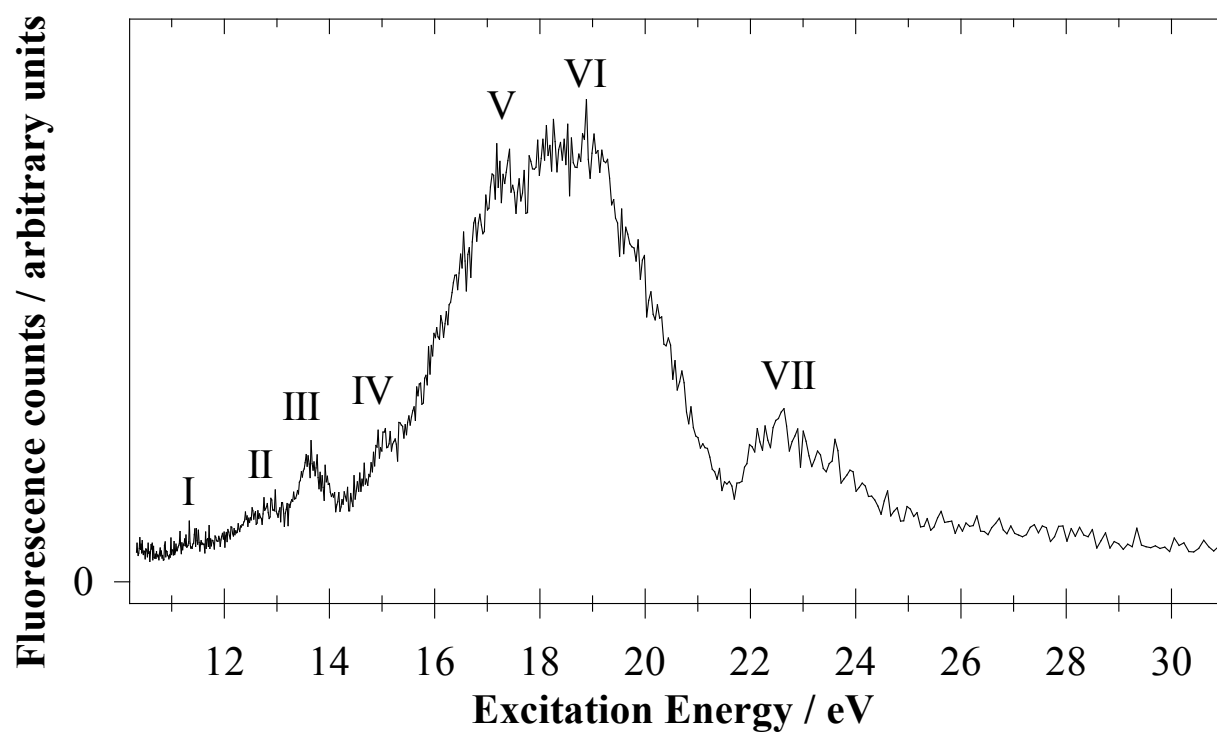
**Fig. 1** A fluorescence excitation spectrum of  $\text{NF}_3$ . This was recorded in Berlin using a spectral resolution of 0.3 nm.

**Fig. 2** Dispersed fluorescence spectra of  $\text{NF}_3$ . The spectral resolution for  $\lambda_2 = 8$  nm.

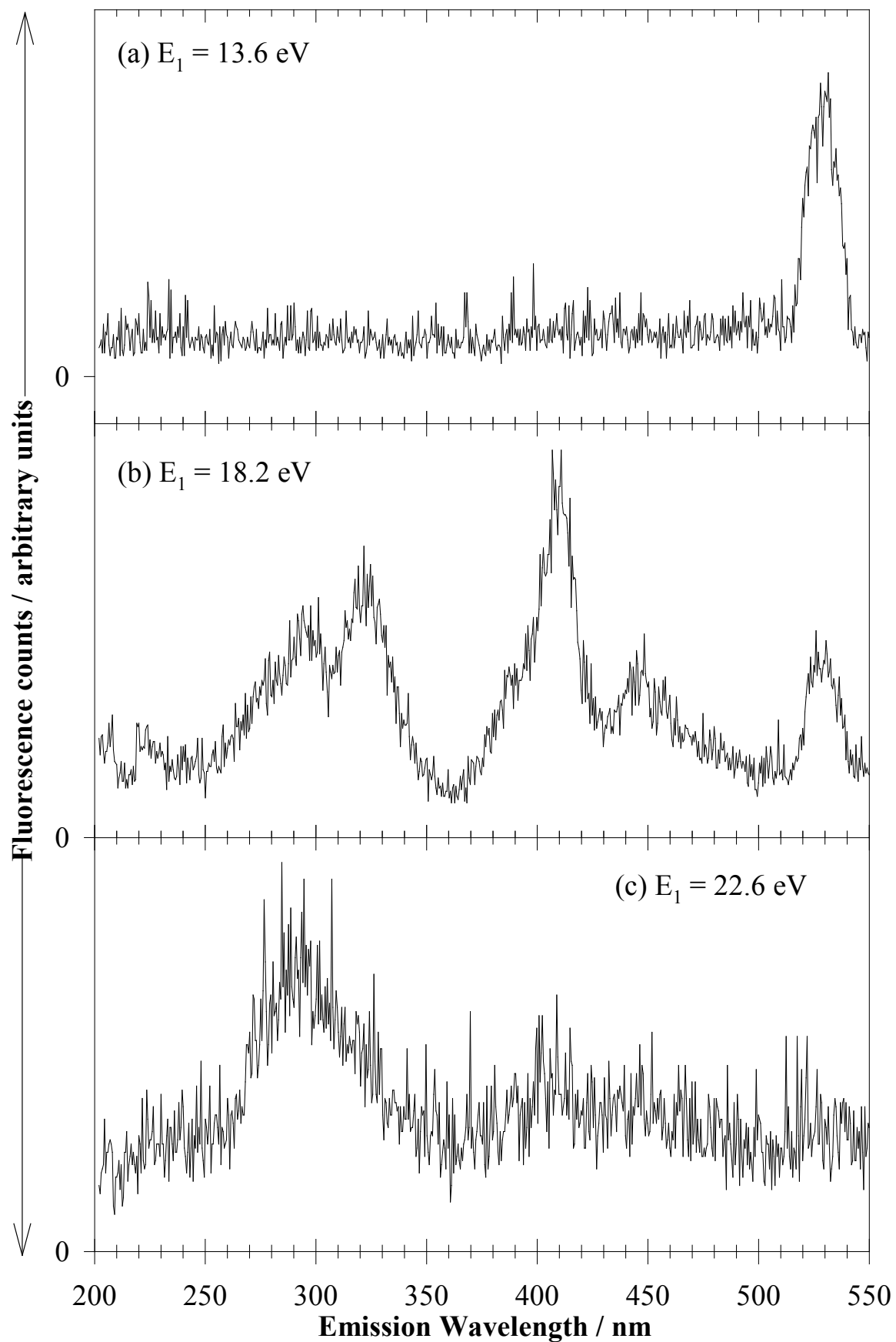
**Fig. 3** Action spectra of  $\text{NF}_3$ . The spectral resolution = 0.3 nm.

**Fig. 4** Action spectra of  $\text{NF}_3$ . The spectral resolution = 0.3 nm.

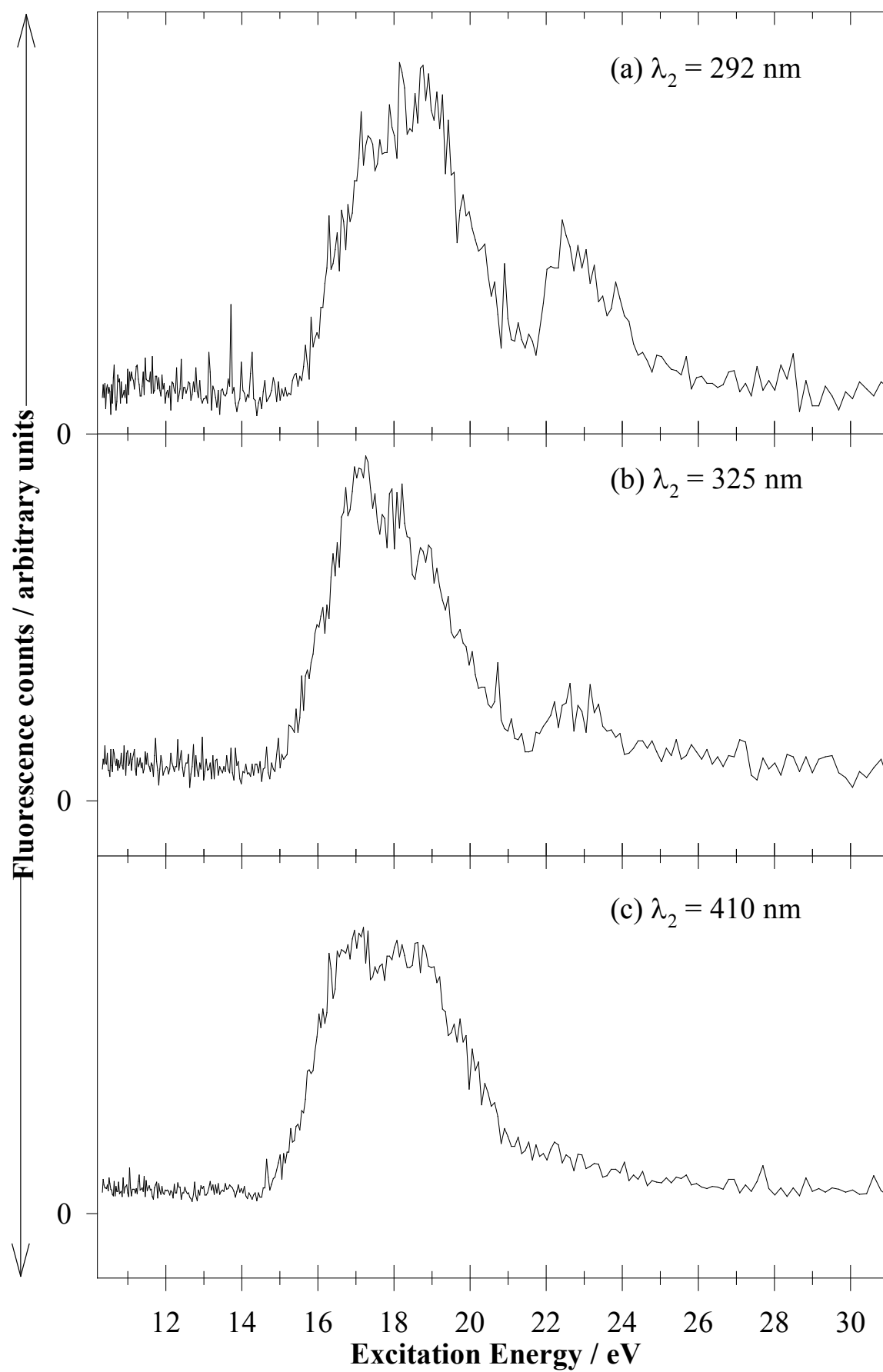
**Fig. 5** Measurement of the lifetimes of  $\text{NF}_2^*$  and  $\text{NF } b^1\Sigma^+$ . Resolution is 0.4134 ns / channel.



**Fig. 1**

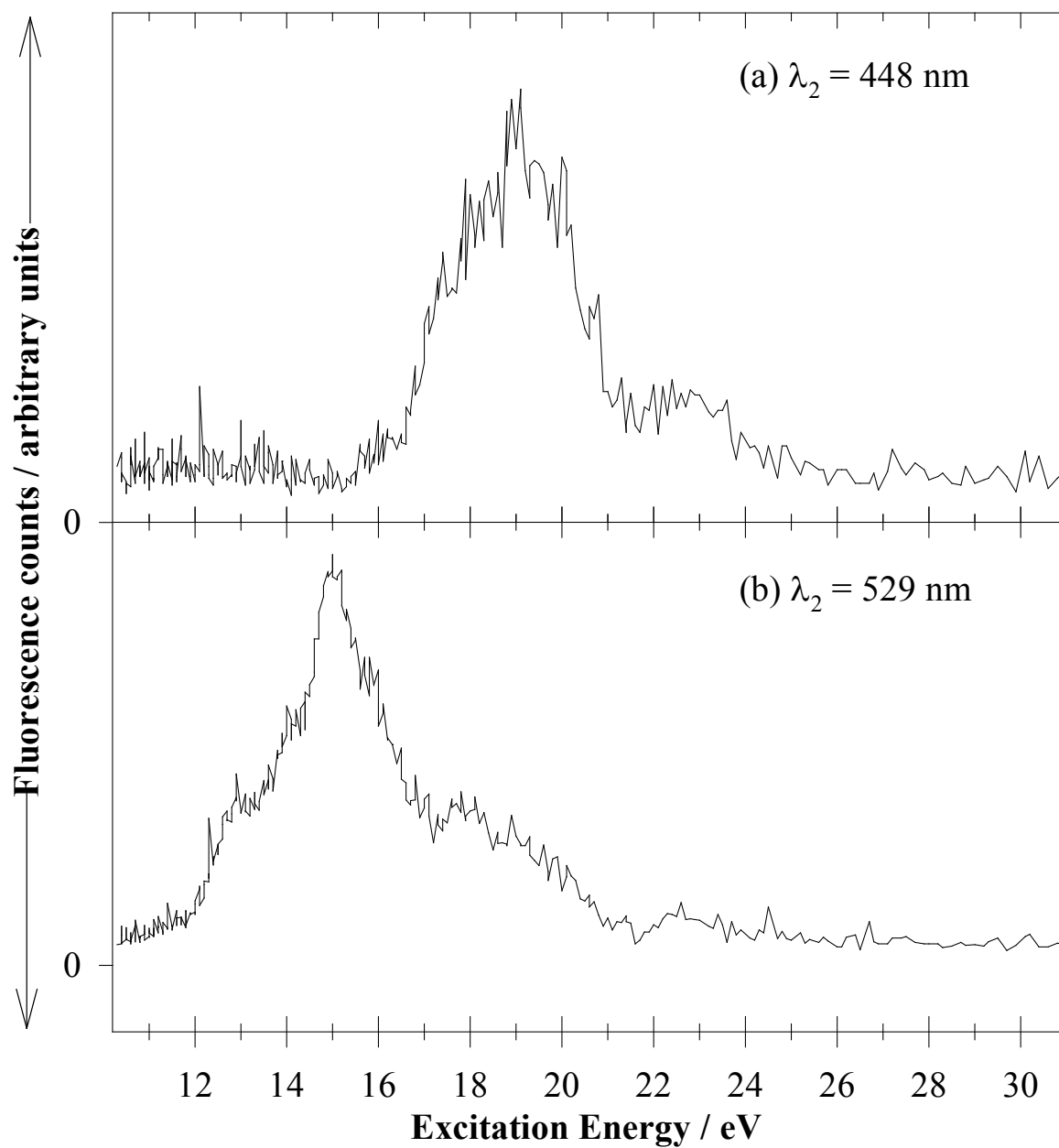


**Fig. 2**



**Fig. 3**





**Fig. 4**

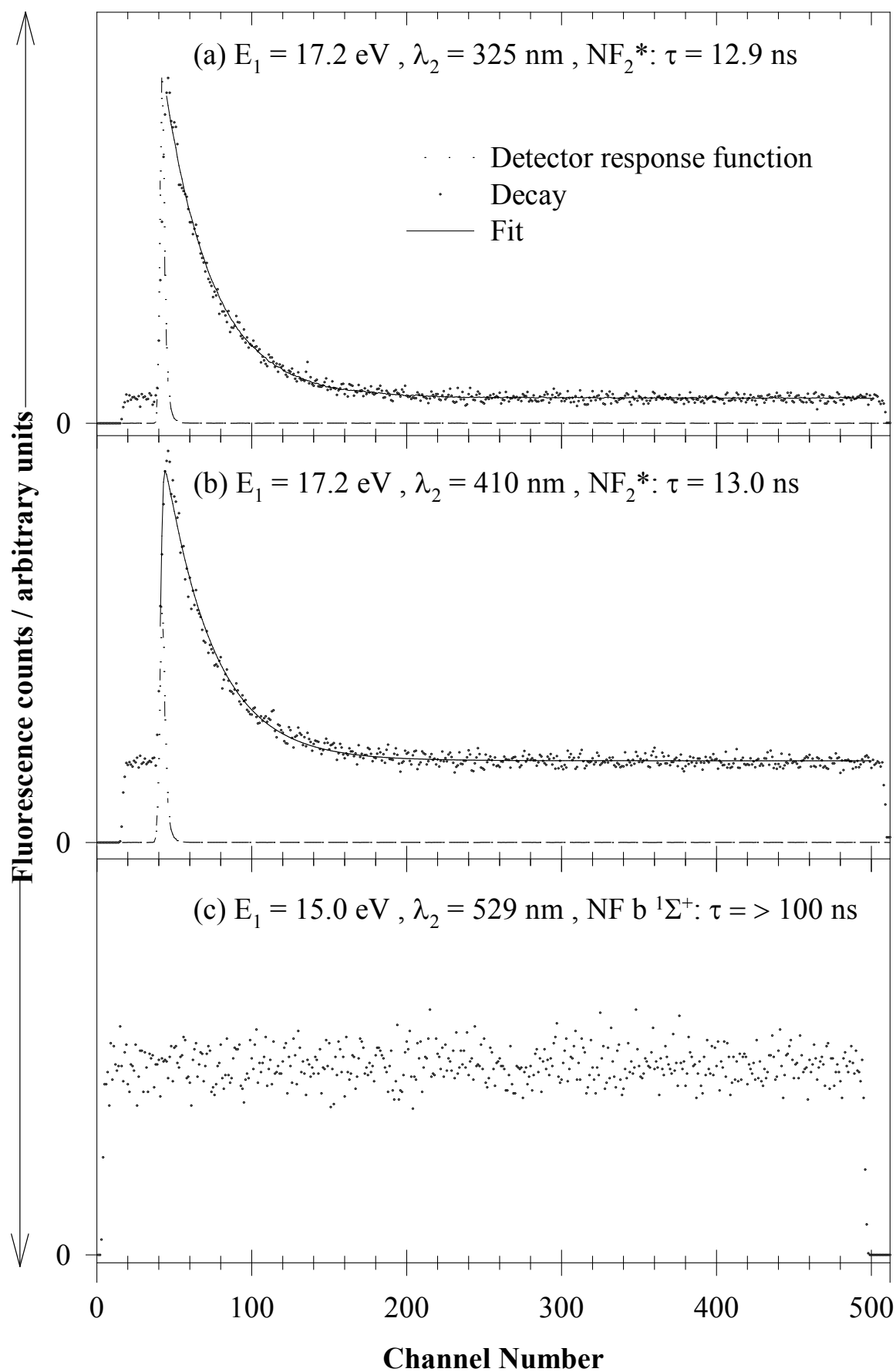


Fig. 5